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54 Diode and metal stud therefor.

57 A diode according to the invention comprises an electrically insulating envelope (2), within which a wafer (1) of semiconductor material with a pn junction is enclosed between metal studs (3, 4). The metal studs (3, 4) are sinter bodies mainly comprising tungsten, a metallic sintering activator and a material chosen from the group comprising Y_2O_3 , SiO_2 , Al_2O_3 , ZrO_2 and ThO_2 . The metal studs (3, 4) can be manufactured at a comparatively low temperature and nevertheless have a very high density and a very great strength as well as a fine structure.

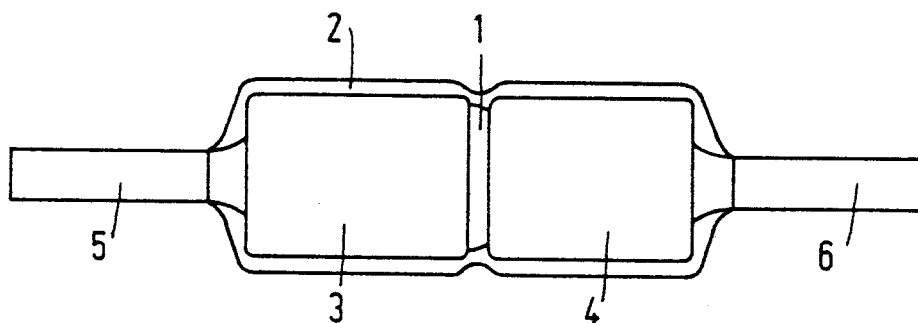


FIG.1

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"Diode and metal stud therefor."

The invention relates to a diode comprising an electrically insulating envelope, within which a semiconductor wafer with a pn junction is enclosed between metal studs, and current conductors which are connected to a respective metal stud and project beyond the envelope, the metal studs being sinter bodies mainly comprising tungsten and a metallic sintering activator; the invention further relates to a metal stud
5 suitable for use in such a diode. Such a diode is known from Japanese Patent Application 58-75862 A - (Touchou Kinzoku K.K. 1983-5-7).

Before sintering, less than 0.5 % by weight of Ni has been added to the tungsten of the studs of the known diode. The addition renders it possible to sinter the studs at a lower temperature (1800 -1950°C) than is the case in the absence of Ni. Without the addition of Ni, the sintering process should be effected at
10 at least 2200°C in order to be able to accomplish the operation within a reasonable period of about half an hour.

A disadvantage of the use of Ni as sintering activator is that it leads to a considerably coarser structure of the sinter body, as also appears from photographs in the aforementioned Patent Application. It has been found that, when the structure become coarser, this leads to a reduction of the mechanical strength of the
15 metal studs.

It is known from Japanese Patent Application 55-123135 A (Tokyo Shibaura Denki K.K., 1980-9-22) that tungsten sinter bodies can contain Fe or Co as a metallic sintering activator instead of Ni. Furthermore, it has been found that palladium is a suitable alternative.

The invention has for its object to provide (diodes with) sintered metal studs consisting mainly of
20 tungsten, which can be readily manufactured and have a great strength.

According to the invention, this object can be achieved in a diode of the kind described in the opening paragraph and in metal studs suitable for this diode in that the metal studs also contain a material chosen from the group comprising Y_2O_3 , SiO_2 , Al_2O_3 , ZrO_2 and ThO_2 .

It has been found that a small quantity of this addition to the studs leads to a great strength and at the
25 same time to a fine structure of the studs. This is also the case if the metallic sintering activator is present in a quantity which -according to the aforementioned Japanese Patent Application -is no longer permissible, such as 0.5 % by weight or more.

A favourable consequence of the presence of a mentioned oxide is that the metallic sintering activator - (the metal promoting the sintering process) may be present in a comparatively large quantity, for example,
30 in a quantity of 0.1 -2 % by weight, more particularly from 0.2 to 0.8 % by weight. In fact it has been found that a high density of the sintered studs and a great strength can be attained already at considerably lower temperature within a short period. A sintering temperature of about 1500°C, for example 1425 -1600°C, for about 15 to 30 minutes yields a density of 95 % or more of the largest possible density (95 % = 18.3 g/cm³).

The addition of a mentioned oxide substantially does not influence the electrical properties of the studs
35 because a small quantity is sufficient. In general a quantity of 0.1 to 2 % by weight is sufficient. As a rule, a quantity of from 0.2 to 1 % by weight is amply sufficient.

Two embodiments of a diode in accordance with the invention are shown in the drawing in side elevation.

In Figure 1, a wafer 1 of semiconductor material with a pn junction is enclosed within a glass envelope 2
40 between metal studs 3, 4 which are connected to a respective current conductor 5, 6 projecting beyond the envelope. In the embodiment shown, the glass envelope 2 keeps the studs 3, 4 pressed on both sides against the wafer 1.

In Figure 2 parts corresponding to those in Figure 1 are designated by the same reference numerals.
45 The Figure shows a drop diode, in which the glass envelope 12 is in the form of a drop. The studs 3, 4 are connected in this embodiment by means of solder to the wafer 1.

In both Figures the metal studs 3, 4 are sinter bodies mainly comprising tungsten and a metal promoting the sintering process and they also contain a material chosen from the group comprising Y_2O_3 , Al_2O_3 , SiO_2 , ZrO_2 and ThO_2 .

The metal studs were obtained as follows.
50

Tungsten powder was incorporated in a solution of $Ni(NO_3)_2$ in demineralized water. The mixture was shaken for 2 hours and was then dried in vacuo at 100°C. Subsequently, the powder was incorporated in a $Y(NO_3)_3$ solution in water, shaken for 2 hours and then dried in vacuo. The powder was heated in hydrogen at 850°C in order to convert the salts into Ni and Y_2O_3 , respectively. The content of Ni, like that of Y_2O_3 , was 0.5 % by weight.

The powder obtained was mixed with a dry binder, was then incorporated in demineralized water and granulated. The granulate was sieved in order to isolate the fraction of 44 -144 μm .

The granulate was pressed to mouldings, after which the mouldings were decarbonized in hydrogen/water vapour at 1000°C.

5 The mouldings were sintered to form studs by increasing the temperature from 1000°C by 25°C per minute to the final temperature and keeping the mouldings at this temperature for some time.

For comparison, tungsten studs were made in a similar manner which contained only 0.5 % by weight of Ni.

10 Of both types of studs (i.e. containing and not containing Y_2O_3), the density was determined. This density is indicated, expressed in % of the largest possible density, in Table 1. Of those sinter bodies whose density was at least 95.0 % the strength was determined. Table 1 indicates the pressure required for deforming the sinter bodies by 1 %.

Table 1

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sintered at final temperature		1425°C		1500°C		1700°C	
for (min.)		(%)	N/mm ²	(%)	N/mm ²	(%)	N/mm ²
0	0 % Y_2O_3	87.2		93.9		95.7	741
0	0.5% Y_2O_3	92.9		96.3	1264	97.5	1019
15	0 % Y_2O_3	92.2		96.3	797	96.1	699
15	0.5% Y_2O_3	95.2	1262	97.3	1162	97.4	999
30	0 % Y_2O_3	93.9		96.8	774	96.3	705
30	0.5% Y_2O_3	95.0	1265	97.4	1169	97.7	938
60	0 % Y_2O_3	94.6		96.6	775		
60	0.5% Y_2O_3	95.7	1177				

35 It appears from this Table that the studs containing Y_2O_3 always have a higher density than studs manufactured in a similar manner, but not containing Y_2O_3 . It has always been found that the structure of the studs containing Y_2O_3 is considerably finer than that of studs not containing Y_2O_3 .

It further appears from the Table that the studs containing Y_2O_3 have a considerably greater strength than studs manufactured in a similar manner, but not containing Y_2O_3 .

40 It is further apparent from Table 1 that it is very favourable if the studs are sintered at a low temperature in the range from 1425°C to 1500°C. Other metal studs were obtained in a manner slightly differing from the manner used to manufacture those described in Table 1.

45 Tungsten powder was impregnated with $\text{Ni}(\text{NO}_3)_2$ or with $\text{Co}(\text{NO}_3)_2$ and subsequently dried as described herein before. The powder obtained was then impregnated with $\text{Y}(\text{NO}_3)_3$ or with $\text{Al}(\text{NO}_3)_3$ as described hereinbefore and dried at 70°C in vacuo. From the mixture obtained granules having a size of 44 -144 μm were isolated by sieving.

The granules were compressed to mouldings. The mouldings were heated in hydrogen at 850°C in order to convert the salts into Ni, CO, Y_2O_3 and Al_2O_3 respectively.

50 The mouldings were sintered to form studs by increasing the temperature from 1000°C by 25°C per minute to the final temperature and keeping the mouldings for some time.

Of all studs made the density was determined and expressed in % of the largest possible density. The strength of the studs made was judged by determination of the failure load, the pressure at which the studs collapse. This strength is expressed in N/mm².

55 The results are represented in Tables 2 -4. The quantities of Ni, Co, Al_2O_3 and Y_2O_3 are in % by weight.

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Table 2

	sintered at final temp. of 1500°C for (min)	Ni(%)	Y ₂ O ₃ (%)	density(%)	strength (N/mm ²)
15	15	0,25	0,25	97,7	1266
	15	0,5	0,25	97,3	1020
20	30	0,5	0,25	97,0	1011
	15	0,5	0,5	97,2	1250
	30	0,5	0,5	96,7	1265
25	15	0,5	1,0	96,7	1422
	30	0,5	1,0	96,6	1415
30	* 15	0,5	0	95,6	768

* for comparison

35

Table 3

	sintered at final temp. of 1500°C for (min)	Ni(%)	Al ₂ O ₃ (%)	density(%)	strength (N/mm ²)
40	0	0,5	0,5	95,7	1470
	15	0,5	0,5	96,9	1206
45	* 15	0,5	0	95,6	768

* for comparison

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5

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Table 4

15	sintered at final temp. of 1550°C for (min)	Co(%)	Y ₂ O ₃ (%)	density(%)	strength (N/mm ²)
	15	0,5	0,5	95,0	1521
20	30	0,5	0,5	95,6	1564
	*	15	0,5	0	92,8

25 * for comparison

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40 From Table 2 it appears that a quantity of Y₂O₃ as low as 0,25 % by weight suffices to yield studs having a very high density and strength. These parameters are highest in case an equal amount of Ni is present. The density and the strength of all studs are considerably improved as compared to the reference studs, which do not contain Y₂O₃. The structure of studs containing Y₂O₃ is finer than the structure of studs not containing Y₂O₃. The higher ratio's of Y₂O₃ and Ni yield the finer structure.

Table 3 shows that studs having a higher density and a very high strength are obtainable when in addition to Ni Al₂O₃ is present. The studs have much finer structure than studs lacking Al₂O₃.

45 From Table 4 it appears that studs having a much higher density and a very high strength are obtained when Al₂O₃ is added in addition to Co. The studs of the invention have a very fine structure. The density of the reference studs lacking Al₂O₃ is unacceptably low.

50 From studs prepared by sintering tungsten powder containing nickel at 1500°C or cobalt at 1550°C, both during 15 minutes, diodes were manufactured. The electrical conductivity of the diodes was compared with the conductivity of diodes having sintered studs consisting of tungsten and 0,5 % of nickel, and of diodes having studs of drawn tungsten wire. The conductivity, both at 25°C and at 165°C, was measured by determination of the voltage drop over the diodes when a current was passed through the diodes of 1 mA or of 100 mA.

The results of these tests are represented in Table 5.

55

Table 5

5	diode having studs of tungsten and	1 mA		100 mA	
		25°C	165°C	25°C	165°C
	0,5 % Ni 0,5 % Y ₂ O ₃	1,74	0,79	2,45	1,76
10	0,5 % Ni 0,5 % Al ₂ O ₃	1,74	0,79	2,45	1,75
	0,5 % Co 0,5 % Y ₂ O ₃	1,71	0,73	2,44	1,75
	0,25% Ni 0,25% Y ₂ O ₃	1,73	0,78	2,44	1,74
	0,5 % Ni 0,25% Y ₂ O ₃	1,74	0,79	2,45	1,76
15	0,5 % Ni 1 % Y ₂ O ₃	1,74	0,78	2,45	1,75
	* 0,5 % Ni	1,73	0,78	2,45	1,76
20	* tungsten wire	1,75	0,79	2,45	1,74

* for comparison

25 From these data it is concluded that the addition of Y₂O₃ or Al₂O₃ does not significantly influence the electrical conductivity of diodes having studs containing said oxides.

The roughness of the studs according to the invention is always smaller than the maximum permissible roughness of 5 µm.

30 Claims

1. A diode comprising an electrically insulating envelope, within which a wafer of semiconductor material with a pn junction is enclosed between metal studs, and current conductors which are connected to a respective metal stud and project beyond the envelope, the metal studs being sinter bodies mainly comprising tungsten and a metallic sintering activator, characterized in that the metal studs further contain a material chosen from the group comprising Y₂O₃, SiO₂, Al₂O₃, ZrO₂ and ThO₂.

2. A metal stud suitable for the diode claimed in Claim 1 comprising a sinter body mainly comprising tungsten and the metallic sintering activator, characterized in that the metal studs further contain a material chosen from the group comprising Y₂O₃, SiO₂, Al₂O₃, ZrO₂ and ThO₂.

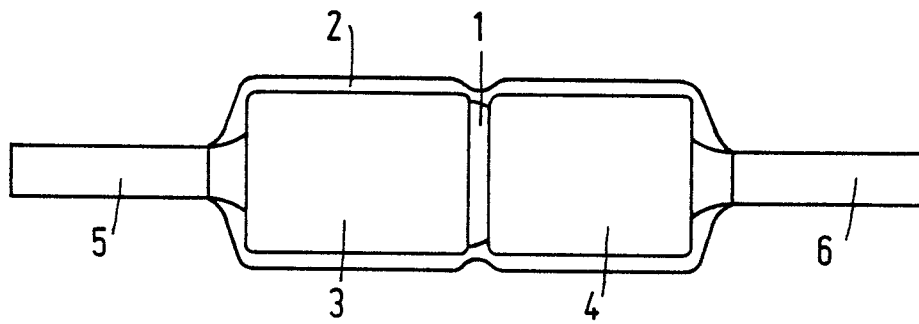


FIG.1

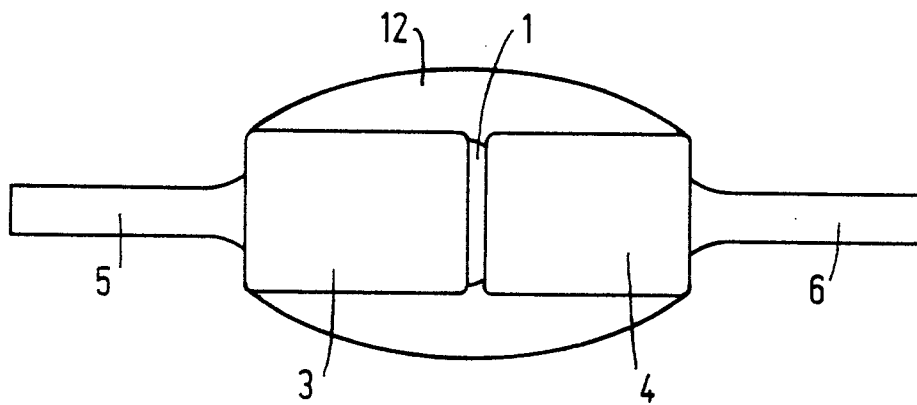


FIG.2



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-3 996 602 (GENERAL INSTRUMENT) * Column 4, lines 22-27 *	1,2	H 01 L 23/48 C 22 C 32/00
Y	DE-A-1 533 395 (TOKYO SHIBAURA) * Claim 1 *	1,2	
A	US-A-3 551 992 (BATTELLE) * Claims 1,2 *	1,2	
A	GB-A-1 209 969 (WIELAND) * Claims 1,4 *	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26-01-1987	Examiner DE RAEVE R.A.L.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			